REP 1993-025

Journal of Chromatography, 634 (1993) 289–296
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 816

Gas chromatographic determination of sodium monofluoroacetate as the free acid in an aqueous solvent

Bruce A. Kimball* and Elizabeth A. Mishalanie☆

United States Department of Agriculture, Animal and Plant Health Inspection Service, Denver Wildlife Research Center, Building 16, Denver Federal Center, Denver, CO 80225 (USA)

(First received August 14th, 1992; revised manuscript received December 15th, 1992)

ABSTRACT

A procedure was developed for the determination of sodium monofluoroacetate as the free acid by capillary gas chromatography with mass-selective detection. Commercially available polyethylene glycol capillary columns were compatible with injections of highly acidic aqueous solutions which were required for this relatively strong acid. Using monochloroacetic acid as an internal standard, a coefficient of variation of less than 2% was routinely obtained from replicate injections of a 100 μg/ml solution of sodium monofluoroacetate in 1 *M* HCl. The monofluoroacetic acid/monochloroacetic acid detector response ratio was a linear function of sodium monofluoroacetate concentration from 5 to 200 μg/ml. Since derivatization is not required and mass spectrometric identification of monofluoroacetic acid is obtained, the method offers advantages over previously described chromatographic methods for the determination of sodium monofluoroacetate. The average analyte recovery from 30 to 40 g biological samples fortified with between 2.5 and 100 mg of sodium monofluoroacetate was 81% with relative standard deviation typically less than 7%. The instrument limit of detection was 200 pg sodium monofluoroacetate when the detector was operated in the selected ion monitoring mode.

INTRODUCTION

Sodium monofluoroacetate (CH_2FCO_2Na) has been used as a vertebrate pesticide for more than 40 years, and is commonly known as Compound 1080. Its use has been widespread throughout North America, Australia and New Zealand with peak usage in the 1960s. Sodium monofluoroacetate is extremely toxic. The oral LD_{50} (*Rattus fuscipes*) is 1.13 mg/kg [1]. It has been administered for the control of vertebrate pests through several baiting techniques and as a liquid formulation for the protection of livestock from predators. The US Environmental Protection Agency required data concerning sodium monofluoroacetate residues on sheep wool and skin after the liquid formulation was released from livestock protection collars during coyote attacks on sheep.

Because of the extreme toxicity of sodium monofluoroacetate, there has been a need for monitoring low levels of this compound in a variety of matrices. Numerous methods have been developed for the determination of sodium monofluoroacetate in pesticide formulations, tissues, and environmental samples. Since 1980,

* Corresponding author.
☆ Present address: United States Environmental Protection Agency, Office of Enforcement, National Enforcement Investigations Center, Building 45, Denver Federal Center, Denver, CO 80225, USA.

methods have been published based on non-chromatographic techniques such as indirect fluorometric detection [2], ^{19}F nuclear magnetic resonance [3,4], and direct measurement of the fluoride ion [5–7]. Many gas [8–21] and liquid [22,23] chromatographic determinations require pre-column derivatization of monofluoroacetic acid. Although some of these chromatographic techniques are capable of detecting low levels of monofluoroacetic acid, the derivatization procedures are generally complex and time consuming. Esterification is particularly difficult due to the presence of water in the sample extract. Time-consuming drying steps are required and low analyte recoveries are often obtained [17]. An analytical method using ion chromatography was developed in this laboratory for the determination of sodium monofluoroacetate based on the separation and detection of the monofluoroacetate ion [24]. This method has been used to assay sodium monofluoroacetate technicals, manufacturing use products, and aqueous formulations containing sodium monofluoroacetate. A reversed-phase liquid chromatographic method for the determination of the free acid has recently been reported [25]. However, a procedure for the gas chromatographic determination of sodium monofluoroacetate as the free acid has not been reported to date.

Commercially available capillary columns have been shown to be compatible with injections of aqueous samples because of their bonded and crosslinked phases. J & W Scientific presented data [26] describing the DB-FFAP (free fatty acid phase) column's ability to perform the separation of weak fatty acids (C_2–C_7) in water with pK values ranging from 4.7 to 4.9. Using these types of capillary columns with minor procedural modifications, we have developed a procedure for the determination of monofluoroacetic acid, a stronger acid with a pK_a of 2.7. This procedure requires the use of 1 *M* HCl as the sample solvent, which minimizes adsorption problems commonly encountered with the chromatographic determination of free acids in aqueous solutions. The gas chromatographic procedure described below does not require a derivatization procedure, provides high-resolution separations, and allows for selective detection of monofluoroacetic acid.

EXPERIMENTAL

Apparatus

A Hewlett-Packard Model 5890 gas chromatograph equipped with a Hewlett-Packard 5970 series mass-selective detector was used for this work. The mass-selective detector was equipped with a Model 270 Granville-Phillips ion gauge and controller to monitor pressure in the ion source which was typically $4 \cdot 10^{-5}$ Torr (1 Torr = 133.322 Pa). The electron impact ionization energy was 70 eV.

Octadecyl silane solid-phase extraction (SPE) columns (J.T. Baker, Phillipsburg, NJ, USA) were used for sample clean-up.

A capillary guard column was required when solutions of 1 *M* HCl were injected into the gas chromatograph. The guard column was prepared from a fused-silica capillary column identical to the analytical column.

The capillary columns were 15 m × 0.25 mm I.D. with 0.25 μm bonded phases of acidified polyethylene glycol (DB-FFAP; J & W Scientific, Folsom, CA, USA, and Nukol; Supelco, Bellefonte, PA, USA). A helium carrier was used at a linear velocity of 47 cm/s. The use of a lower, more optimum linear velocity was prevented by the pressure drop across the short column created by the capillary direct interface.

Reagents

Sodium monofluoroacetate (97%) and nigrosine black dye were provided by Tull Chemical Co. (Oxford, AL, USA). Tartrazine dye (FD&C Yellow No. 5) was obtained from Ingredient Technology Corp. (Des Plaines, IL, USA). Deionized water was produced in the laboratory and used to prepare all aqueous solutions.

The following solutions were prepared for GC analysis: 10 and 1000 μg/ml acetic, propionic and isocaproic acids in water; 100 μg/ml acetic, propionic and isocaproic acids in ethyl acetate; 100 μg/ml sodium monofluoroacetate in water; 2500 μg/ml sodium monofluoroacetate in 1 *M* HCl; and 100 μg/ml sodium monofluoroacetate in 200 m*M* trifluoroacetic acid (TFA). The calibration standards were 5, 10, 50, 100, 150 and 200 μg/ml sodium monofluoroacetate in 1 *M* HCl with monochloroacetic acid added as an internal standard at a concentration of 50 μg/ml.

To prepare a solution of monofluoroacetic acid in an organic solvent, 1 ml of the 2500 μg/ml sodium monofluoroacetate in 1 *M* HCl solution was subjected to a liquid–liquid extraction with 10 ml of ethyl acetate. Solutions containing only 1 *M* HCl were treated similarly to serve as reagent blanks. Acetic acid was added to the ethyl acetate extracts as an internal standard to give a final acetic acid concentration of 50 μg/ml.

Preparation of capillary guard column

The guard column was prepared by removing 3 cm of the polyimide coating from one end of a capillary column which was identical to the analytical column. A glassblowing torch burning methane and compressed air was used for this procedure. The exposed fused silica was deactivated with a 5% dichlorodimethyl silane in toluene solution and the guard column was cut to a length of 0.5 m. The end of the guard column with the polyimide removed was positioned in the injector so that only deactivated fused silica was exposed in the injection port. Connection to the analytical column was made by a fused-silica low-dead-volume connector (Restek Corp., Bellefonte, PA, USA).

Procedure

Biological samples consisting of sheepskin with attached wool were fortified with an aqueous sodium monofluoroacetate formulation. The formulation consisted of 10 mg/ml sodium monofluoroacetate, 0.05 mg/ml nigrosine black dye and 5 mg/ml tartrazine dye in water. A control formulation (containing no sodium monofluoroacetate) was also prepared and replicate samples were fortified with this solution. The sheepskin/wool samples were cut into 100-cm^2 pieces (approximate mass 30–40 g) prior to fortification and each piece was extracted with 500 ml 1 *M* HCl. Since the samples were fortified with at least 2.5 mg, concentration of the 500-ml extracts was not required. Aliquots (10 ml) of the extracts were then cleaned-up by passing through octadecyl SPE columns. Monochloroacetic acid was added to a known volume of the treated extract as an internal standard to produce a final concentration of 50 μg/ml.

The injection port temperature was 200°C and the transfer line to the mass-selective detector source was maintained at 230°C. The injection mode, oven temperature programs and mass-selective detector parameters are summarized in Table I. Injections were either 1 μl split (100:1) or 1 μl splitless (purge time 0.6 min, split vent flow 80 ml/min). Injections (1 μl) of 7.4 *M* phosphoric acid were made every 5 to 10 injections when solutions of 1 *M* HCl were injected into the gas chromatograph. Sample extracts were filtered through 0.45-μm nylon filters prior to injection. Single point calibrations were used

TABLE I

SUMMARY OF GC AND DETECTOR PARAMETERS

SIM = Selected ion monitoring.

Condition	Injection mode	Oven program	Mass-selective detector
A	Split	135°C isothermal	SIM, *m/z* 41, 43, 45, 55, 57, 60, 74, 87
B	Splitless	85°C (0.5 min) $\xrightarrow{15°C/min}$ 245°C	SIM, *m/z* 41, 43, 45, 55, 57, 60, 74, 87
C	Splitless	85°C (0.5 min) $\xrightarrow{15°C/min}$ 230°C	SIM, *m/z* 61, 78
D	Splitless	60°C (0.5 min) $\xrightarrow{15°C/min}$ 215°C	SIM, *m/z* 41, 43, 45, 55, 57, 60, 74, 87
E	Splitless	60°C (0.5 min) $\xrightarrow{15°C/min}$ 215°C	Scan, *m/z* 15→80 SIM, *m/z* 60, 78
F	Splitless	110°C (0.5 min) $\xrightarrow{15°C/min}$ 240°C	SIM, *m/z* 61, 78
G	Splitless; guard column	110°C $\xrightarrow{15°C/min}$ 200°C	SIM, *m/z* 50, 78

for the quantitation of sodium monofluoroacetate in the sample extracts.

RESULTS AND DISCUSSION

Various solvent systems were investigated to identify a solvent that would (1) convert the sodium salt to the free acid, (2) provide for adequate chromatographic performance of monofluoroacetic acid and (3) be useful as an extraction solvent for complex matrices. Each solvent system is described and discussed below.

Free acid–water solutions

Aqueous solutions of acetic, propionic and isocaproic acids were used to verify the performance of the capillary columns under the conditions recommended by the column manufacturers. The columns from two manufacturers exhibited good resolution of the three acids under isothermal conditions when split injections were made (Table I, condition A). Injection of a water reagent blank after the sample solutions did not result in chromatographic responses from these acids.

Splitless injections of these solutions were then investigated. In order to retain chromatographic performance of the free acids, adjustment of the oven temperature program was required (Table I, condition B). Injections of a 10-μg/ml solution of the acids under these conditions resulted in a chromatographic separation similar to that observed in the split mode. However, injections of water after the sample solutions produced chromatographic responses for each of the acids. These "ghost peak" responses may have been the result of adsorption and desorption processes in the injection port. Polar compounds such as free acids exhibit an affinity for active sites in the injection port. Adsorption may also occur at active sites on the head of the column. Highly polar solvents such as water can then desorb the acids from the active sites. Consequently, the performance of the chromatographic system was acceptable under the conditions specified by the column manufacturers, but was not acceptable under conditions that would be needed for residue determinations.

Because less than 1% of the monofluoroacetate is protonated in a 100 μg/ml sodium monofluoroacetate in water solution, sodium monofluoroacetate in water solutions could not be chromatographed under conditions similar to the free acid in water solutions (Table I, condition C). No chromatographic responses were observed after numerous injections of a 100 μg/ml sodium monofluoroacetate in water solution. However, when a single injection of 1 *M* HCl was made after injection of the sodium monofluoroacetate in water solution, a monofluoroacetic acid response was observed. Repeat injections of the sodium monofluoroacetate in water solution following injection of 1 *M* HCl resulted in a chromatographic response for monofluoroacetic acid, but the peak shape rapidly deteriorated with subsequent injections. Apparently, the injection of HCl resulted in the formation of the free acid from the non-volatile salt remaining in the injection port. This also produced an acidic environment which promoted the formation of the free acid in subsequent injections of sodium monofluoroacetate in water. As more injections of sodium monofluoroacetate/water solution were made, the effect of the acid diminished until a monofluoroacetic acid response was no longer observed.

Free acid–ethyl acetate solutions

Splitless injections of the 100-μg/ml standard solution of acetic, propionic and isocaproic acids in ethyl acetate were followed by splitless injections of water or ethyl acetate (Table I, condition D). Only the injection of water resulted in ghost peak responses for the three acids. Similar to previous observations, split injections of the free acids–ethyl acetate solution followed by split injections of water did not result in chromatographic responses. These observations indicate that the increased residence time of the analyte and solvent in the injection port during splitless injections and solvent polarity lead to the appearance of the ghost peaks.

In addition to the solvating power and residence time of the solvent, the adsorption/desorption behavior of weak acids is also a function of the analytes' acid strength and the rate of gas–solid collisions which lead to adsorption. For example, the splitless injection of water pro-

duced larger ghost peak responses for monofluoroacetic and monochloroacetic acids relative to the weaker acetic acid. The rate of adsorption of a gas to a solid surface is determined by the sticking coefficient and the rate of gas–solid collisions. This collision rate has an inverse square root relationship with molecular mass. This influence is exhibited in the splitless injection of water induced desorption responses of acetic (pK_a 4.7), propionic (pK_a 4.9) and isocaproic (pK_a 4.8) acids. Although they are similar in acid strength, the ghost peak response of acetic acid is larger in relation to the ghost peak responses of the more massive propionic acid which is in turn larger than the response of isocaproic acid.

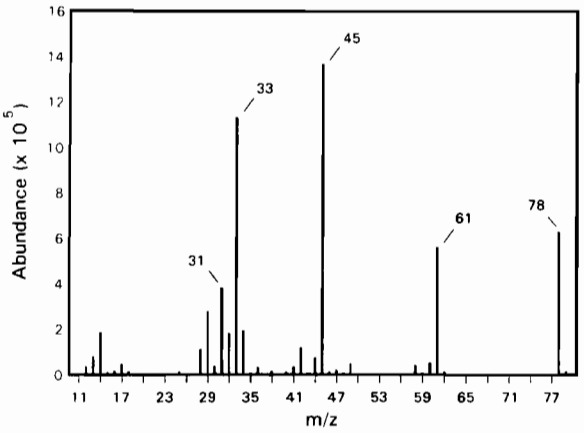

Fig. 1. Mass spectrum of monofluoroacetic acid. m/z 31 = fragment FC^+; m/z 33 = FH_2C^+; m/z 45 = $HO–C=O^+$; m/z 61 = $FH_2C–C=O^+$; m/z 78 = M^+.

Monofluoroacetic acid–ethyl acetate solutions

In an effort to eliminate the adsorption/desorption behavior observed with the water solvent system, an organic solvent was investigated. Monofluoroacetic acid was partitioned into ethyl acetate by liquid–liquid extraction of a sodium monofluoroacetate–1 *M* HCl solution, resulting in a solution of monofluoroacetic acid in acidified ethyl acetate. Based on calculations using the pK_a of monofluoroacetate, 1 *M* HCl should protonate >99.9% of the monofluoroacetate. Splitless injections of the monofluoroacetic acid–ethyl acetate solutions (Table I, condition E), resulted in a good chromatographic response for monofluoroacetic acid. Acetic acid was added to the ethyl acetate solution for use as an internal standard and also exhibited good chromatographic behavior. However, when reagent blanks (ethyl acetate extract of 1 *M* HCl) containing the internal standard were injected, a monofluoroacetic acid response was observed. This ghost peak response persisted for numerous subsequent injections of the reagent blank. The signal was identified as a monofluoroacetic acid response by its mass spectrum (Fig. 1). Syringe carryover was eliminated as the source of the ghost peak by use of separate syringes for injecting standard solutions and blanks. Since the only source of monofluoroacetic acid was the standard solutions, it was apparent that the free acid was being desorbed from the injection port and/or the head of the column as described previously. Injection port liners were silanized or phosphorylated in an attempt to eliminate the liner as the source of active sites in the injection port. These procedures did not eliminate observance of ghost peaks responses. However, phosphorylation of the stainless steel seal in the injection port did temporarily eliminate the ghost peak responses. Apparently, the small amount of water which partitioned into the ethyl acetate promoted desorption of the acids from the injection port. Attempts to dry the ethyl acetate extract by centrifugation or addition of sodium sulfate did not eliminate the ghost peaks.

Sodium monofluoroacetate–TFA solutions

The monofluoroacetic acid–ethyl acetate data indicated that neither physical nor chemical attempts to eliminate water from ethyl acetate produced the desired effect. A TFA (pK_a 0.3) solvent system was pursued in an attempt to eliminate or minimize the adsorption/desorption behavior of monofluoroacetic acid. TFA could provide a sufficiently acidic environment to protonate monofluoroacetate and also buffer sample extracts. However, since it is also a free acid, TFA caused a chromatographic interference during injections of a 100 μg/ml sodium monofluoroacetate in 200 m*M* aqueous TFA solution (Table I, condition F), and this approach was not pursued further.

Sodium monofluoroacetate–1 M HCl solutions

Since 1 *M* HCl was an effective solvent for desorbing monofluoroacetic acid present in the injector system, it was investigated for use as an injection solvent. As a sample extraction solvent, this solution was also sufficiently acidic to provide sample extracts with a pH similar to the standard solutions. This would allow for direct quantitative comparison of standard and sample solutions.

The corrosive nature of this solvent necessitated some procedural changes which were designed to protect the analytical column. In addition to keeping the initial oven temperature above 100°C to prevent condensation of the corrosive solvent on the head of the column, the guard column was used to further prevent permanent damage to the analytical column. Removal of the polyimide coating from the capillary column was necessary because the 1 *M* HCl reacted with the polyimide exposed in the hot injection port. These procedures allowed for prolonged use of 1 *M* HCl as an injection solvent. The chromatographic performance of monofluoroacetic acid was retained with these changes (Table I, condition G). However, elimination of the solvent effect deteriorated the chromatographic performance of the internal standard, acetic acid. Monochloroacetic acid was chosen to replace acetic acid as the internal standard. Fig. 2 shows a typical chromatogram of a 1 *M* HCl solution containing sodium monofluoroacetate and monochloroacetic acid under these conditions.

Although the use of 1 *M* HCl as the injection solvent resulted in excellent chromatography, the desorption of the free acid continued to produce ghost peaks. Following 20 to 30 injections of a solution of 100 μg/ml sodium monofluoroacetate and 50 μg/ml monochloroacetic acid in 1 *M* HCl, a decreasing trend was observed in the monofluoroacetic acid/monochloroacetic acid detector response ratio. The injection of reagent blanks also resulted in chromatographic responses from the two acids.

Since phosphoric acid had previously been shown to deactivate the injection port, a 1-μl injection of 7.4 *M* H_3PO_4 was made after every 5 to 10 injections of standard solutions or samples. This procedure prevented the occurrence of ghost peaks in reagent and matrix blanks. H_3PO_4 was an excellent solvent for desorbing weak acids which had been previously adsorbed and prevented the adsorption of weak acids in subsequent injections. As expected, phosphoric acid (or pyrophosphoric acid which is present at the injection port temperature of 200°C) damaged the guard column. Typically, we observed deterioration of chromatographic performance after approximately 50 injections of H_3PO_4. Replacement of the guard column restored chromatographic performance. No visible corrosion or other damage to the mass-selective detector source was evident after several hundred injections of acidic aqueous solutions. In addition, the quadrapole tuning parameters did not indicate damage to the source components.

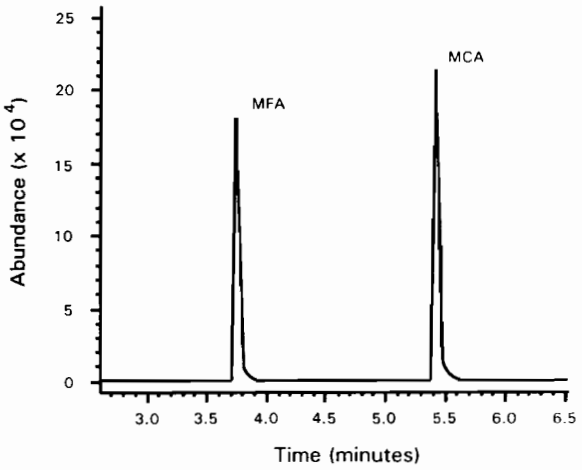

Fig. 2. Monofluoroacetic acid (MFA) and the internal standard monochloroacetic acid (MCA) in 1 *M* HCl (Table I, condition G).

Selectivity, bias and repeatability

Three replicate sheepskin/wool samples fortified with the control formulation and nine sheepskin/wool samples fortified with the sodium monofluoroacetate containing formulation were extracted with 1 *M* HCl to remove the sodium monofluoroacetate residues. The pH values of the sample extracts were less than 0.5 which allowed for direct quantitative comparison to standard solutions of sodium monofluoroacetate in 1 *M* HCl. No chromatographic interfer-

ences were observed from the extraction of the control samples. Recoveries of sodium monofluoroacetate from samples fortified at 2.5, 50 and 100 mg were 85.5% (S.D. = 2.2%, $n = 3$), 80.0% (S.D. = 5.8%, $n = 3$) and 76.7% (S.D. = 2.5%, $n = 3$) respectively. An analysis of variance performed on these data demonstrated that recovery did not vary significantly at the three fortification levels. The lack of available wool and skin samples precluded the analysis of more than three replicate fortified samples.

Response linearity and limit of detection

Repeated injection of a 100 μg/ml sodium monofluoroacetate and 50 μg/ml monochloroacetic acid in 1 *M* HCl solution typically produced detector response ratios with a relative standard deviation of less than 2% from 5 consecutive injections. Response linearity was demonstrated with two sets of six calibration standards. The sodium monofluoroacetate concentration in the calibration standards ranged from 5 to 200 μg/ml, and the internal standard concentration was held constant at 50 μg/ml. Each solution was injected in triplicate. The monofluoroacetic acid/monochloroacetic acid detector response ratio was plotted as a function of sodium monofluoroacetate concentration and a linear regression analysis was performed on the 36-point data set.

Regression analysis generated a *y*-intercept of 0.002 and a slope of 0.007. The standard error of the *y*-intercept was 0.003 and the standard error of the slope was 0.00002. The coefficient of determination (r^2) was 0.9996 which indicates a linear relationship. Applying a 95% confidence interval to the *y*-intercept data, it is found that the *y*-intercept is not significantly different from zero. Therefore, these data demonstrate that a linear relationship exists between detector response ratio and sodium monofluoroacetate concentration and that the ratio can be assumed to be directly proportional to concentration over the investigated range. As a result, a single-point calibration was used to quantitate solutions containing 5–200 μg/ml sodium monofluoroacetate.

The instrument limit of detection (ILOD) was estimated from a monofluoroacetic acid chromatographic response which was approximately 10 times greater than the peak-to-peak noise in the baseline of a chromatogram from a standard solution. The ILOD was defined as the amount of monofluoroacetic acid which would produce a response corresponding to three times the peak-to-peak noise. The instrument limit of detection was determined to be 200 pg sodium monofluoroacetate (200 ng/ml) when the mass-selective detector was operated in the SIM mode (Table I, condition G).

Quality control results from sample analysis

This methodology was used for the determination of sodium monofluoroacetate residues on sheepskin/wool samples collected during a pes-

TABLE II

RECOVERY OF SODIUM MONOFLUOROACETATE FROM QUALITY CONTROL SAMPLES

30- to 40-g wool and skin samples fortified with 50 mg sodium monofluoroacetate.

Replicate	Run							
	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)	7 (%)	8 (%)
1	83.2	81.6	88.3	76.8	79.8	76.3	89.4	85
2	85.7	79.5	87.7	97.3	79.7	76.4	91.8	77
3	87.6	82.0	85.1	85.8	–	84.5	87.2	82
4	–	–	–	–	–	–	101	–
Mean %	85.5	81.0	87.0	86.6	79.8	79.1	92.4	81
S.D. (%)	2.2	1.3	1.7	10.3	–	4.7	6.1	4
R.S.D. (%)	2.6	1.6	2.0	11.9	–	5.9	6.6	5

ticide registration study. Each time a set of samples was analyzed, replicate quality control samples were fortified with 50 mg sodium monofluoroacetate. Analyte recovery for these samples is presented in Table II. Mean recoveries of sodium monofluoroacetate from the quality control samples were in good agreement with the recovery observed during method development. The increased variability in the quality control data from run 4 was attributed to deterioration of the guard column. Replacement of the guard column led to improved precision. The cause of one high recovery value (run 7) was not identified.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Peter J. Savarie for providing the biological samples and Margaret Goodall and Doreen McHugh for providing the quality control data.

Mention of commercial products is for identification only and does not constitute endorsement by the USA Government.

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